Closed-Loop Recycling of Plastics Enabled by Dynamic Covalent Diketoenamine Bonds

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Abstract

Recycled plastics are low-value commodities due to residual impurities and the degradation of polymer properties with each cycle of re-use. Plastics that undergo reversible polymerization allow high-value monomers to be recovered and re-manufactured into pristine materials, which should incentivize recycling in closed-loop life cycles. However, monomer recovery is often costly, incompatible with complex mixtures, and energy-intensive. Here, we show that next-generation plastics—polymerized using dynamic covalent diketoenamine bonds—enable recovery of monomers from common additives, even in mixed waste streams. Poly(diketoenamine)s "click" together from a wide variety of triketones and aromatic or aliphatic amines, yielding only water as a byproduct. Recovered monomers can be re-manufactured into the same polymer formulation, without loss of performance, as well as other polymer formulations with differentiated properties. The ease in which poly(diketoenamine)s can be manufactured, used, recycled, and re-used—without losing value—points to new directions in designing sustainable polymers with minimal environmental impact.

Closed-Loop polymer life cycles are critical to sustainability efforts worldwide.[1–7] Their integration into the global materials ecosystem hinges on maintaining high value in recovered materials at the end of a product's life.

Value is lost when processing is costly, energy-intensive, or alters the physical properties and appearance of recovered materials.[8] To reduce the cost and energy intensity of depolymerizing plastics, lowering the energetic barrier to bond-cleavage is critical. Advances in catalysis[9] and dynamic covalent chemistry[10] have emerged as potential solutions.[11–35] In particular, dynamic covalent polymers known as vitrimers have been recently proposed as sustainable replacements for non-recyclable thermoset materials.[27–35] Vitrimers undergo associative bond exchange reactions in the solid-state, allowing cross-linked materials to be thermally processed and recycled like thermoplastics while maintaining high cross-link density. In certain cases, vitrimers have been shown to depolymerize, yielding soluble oligomers or small molecules (Supplementary Fig. 1). [28,30–32,34,35] However, like other plastics, it remains a challenge to depolymerize vitrimers at low temperatures, in short reaction times, with high tolerance to additives, and from mixed plastic waste streams. Furthermore, depolymerization efforts have not emphasized a return to the original monomers, which limits re-formulation opportunities by requiring further manipulation before re-entering the supply chain.

Here we show that dynamic network polymers synthesized using diketoenamine bonds address these challenges by leveraging their unique chemistry to uncouple the otherwise conflicting demands for formulation, manufacturing, performance, recycling, re-manufacturing, and re-use. Poly(diketoenamine)s, or PDKs, are prepared via “click”[36] polycondensation

reactions between ß-triketones and aromatic or aliphatic amines (Fig. 1). Notably, ß-triketone monomers are accessed in a single step from widely available polytopic carboxylic acids and 1,3-diones.[37] In contrast to other vitrimer platforms (Supplementary Fig. 1), PDKs hydrolyze in strong aqueous acid (0.5–5.0 M H_2SO_4), at ambient temperature, to yield pure, immediately reusable triketones (Supplementary Fig. 2); amine monomers are then recovered using a regenerative resin-based process, closing the loop (Fig. 2a, Supplementary Fig. 3). In 5.0 M H_2SO_4 complete depolymerization occurs in less than 12 h, and pure triketone and amine monomers are recovered in >90% isolated yields (Fig. 2b–d); 5.0 M HCl was similarly effective in PDK depolymerization. Under the same conditions, depolymerization is not observed for common plastics in use today, allowing PDKs to be easily separated from mixed plastic waste streams (Fig. 2e). PDK depolymerization also tolerates a wide spectrum of additives, including dyes, pigments, inorganic fillers, fiber reinforcing fabrics, and flame-retardants, even when these additives comprise high weight-fractions in the polymer composite. Recovered monomers can be re-manufactured without loss of performance, or re-formulated with differentiated properties. The ease in which PDKs can be manufactured, used, recycled, and re-used—without losing value—suggests exciting new paths for next-generation plastics with minimal environmental impact.

Results

Polymer synthesis

The PDK platform encompasses a broad range of polymer formulations for accessing diversity-oriented structure–property space. To begin to explore PDK structure–property space, we prepared three triketone dimers from adipic acid (**TK-6**), suberic acid (**TK-8**), and sebacic acid (**TK-10**) precursors (Fig. 3). Owing to the spontaneous reaction between amines and triketones, PDK networks are easily synthesized by mechanically grinding triketone monomers with *tris*(2-aminoethylamine) (TREN), or with mixtures of TREN and various diamines using a ball mill, without requiring organic solvents. In addition to being a scalable process, we hypothesized that the extent of reaction between amines and triketones could be controlled by adjusting the ball-milling time. To demonstrate this, **TK-6** was ball-milled in the presence of TREN, without solvent, yielding fine powders of network polymer **PDK-6(TREN)** (Supplementary Fig. 4). The T_g, and insoluble (gel) fraction of **PDK-6(TREN)** were measured as a function of both the duration of ball-milling, and equivalents (Eq.) of amine relative to triketone functional groups (Fig. 3e–f). **PDK-6(TREN)** network materials showed high T_g (> 120 ˚C) and gel fractions > 95% in less than 1 h of mechanical processing. The extent of reaction was further analyzed by solid-state NMR spectroscopy, showing no detectable **TK-6** starting material after only 45 min of ball-milling for formulations with ≥ one equivalent of amine (Supplementary Figs. 5–9). The reproducible trajectories of both T_g and gel fraction as a function of

formulation and processing time is an advantage over batch processes where these cannot be controlled, indicating ball-milling is a powerful new tool for controlling network density in dynamic soft matter.

Polymer compounding, de-coloration, and recovery of virgin-quality monomer

We found ball-milling effective in blending into the polymers various stabilizers, plasticizers, dyes, pigments, and flame-retardants, to meet aesthetic, performance, and regulatory requirements without complicating recycling. To demonstrate this, network polymer **PDK-6(TREN**) was recycled as a mixture of colored plastics containing organic and inorganic colorants (Fig. 4). Red, blue, yellow, and black samples **of PDK-6(TREN)** were mixed together and depolymerized in 5.0 M H_2SO_4 to yield a precipitate containing **TK-6** monomer along with carbon nanofibers, TiO_2, and red, blue, and yellow dye molecules. From complex mixtures, triketone monomers are easily separated from additives, and other polymers, by extracting into aqueous base, filtering off insoluble components, and subsequently precipitating triketones upon re-acidification (pH < 3) (Fig. 4 c–d).

Closed-loop recycling of flame-retardant fiber-reinforced composites

Depolymerization strategies, such as ours, are attractive for recycling fiber-reinforced composite materials,[31,32] and PDKs may be particularly well suited

for these applications. To demonstrate the ease of depolymerization and separation of all components in such composites, woven fiberglass was impregnated with a **PDK-6(TREN)** resin containing 25% (*w/w*) triphenylphosphate (TPP) as a flame retardant (Supplementary Fig. 10). The fiber-reinforced composite was subjected to the aqueous processing sequence described above (depolymerize, extract, precipitate), which allows triketone, flame retardant, and fiber reinforcing fabric to be recovered (Fig. 4g–j). Specifically, the initial depolymerization of the PDK resin allows the fiberglass cloth to be removed as a single, undamaged component leaving behind a mixture of **TK-6** monomers and TPP. The triketone monomer is separated from TPP by extracting it into base and precipitating it using acid —effectively separating and isolating pristine fiber material, resin monomer, and flame retardant (Fig. 4j).

Recovery of virgin-quality monomer enables up-cycling

It’s noteworthy that **TK-6** monomer obtained from each of the recycling experiments showed no detectable side products, residual amine, pigments, or flame-retardant additives (Supplementary Figs. 10 & 11). The recovery of pure TK monomers enables immediate re-use for synthesizing new polymers of the same or different formulation, thus maximizing the inherent value of waste material. To demonstrate that recovered triketone monomers can be re-formulated into PDKs with the same, or differentiated properties, we synthesized **PDK-6(TREN)** from recycled **TK-6** as well as network polymers

PDK-6(TREN:ODA) and **PDK-6(TREN:PPG)** using mixtures of TREN and 4,4'-dioxyaniline (ODA) or poly(propylene glycol) *bis*(2-aminopropyl ether) (PPG, M_n = 2000 g mol^{-1}), respectively (Fig. 5). Dynamic mechanical analysis (DMA) of recycled **PDK-6(TREN)** shows nearly identical properties to **PDK-6(TREN)** synthesized from pristine **TK-6** (Fig. 5b). The storage moduli of re-formulated PDK materials range from 0.3 (± 0.1) GPa for **PDK-6(TREN:PPG)** to 1.8 (± 0.2) GPa for **PDK-6(TREN:ODA)** (Supplementary Fig. 11). Formulation chemistry whereby linear polymeric diamines are embedded into PDK networks further allows their ductility to be readily tuned: e.g., incorporation of only 5 mol% poly(tetrahydrofuran) *bis*(3-aminopropyl ether) (M_w ~ 1000 g mol^{-1}) into **PDK-10(TREN)** networks improved the toughness of PDKs without significantly sacrificing room temperature storage and tensile moduli (Fig. 5d–e).

Dynamic covalent diketoenamine bond exchange with aliphatic and aromatic amines

The ability to formulate dynamic covalent network polymers with both aliphatic and aromatic amine monomers is unusual, and a direct consequence of diketoenamine bond-exchange energetics.[38] Kinetic analysis of the diketoenamine bond-exchange revealed remarkably low, catalyst-free activation energies for associative bond exchange: 29 (± 0.9) kJ mol^{-1} for aliphatic amine exchange; and 62 (± 2) kJ mol^{-1} for aromatic amine (aniline) exchange (Supplementary Figs. 13–15). We found that PDK network

polymers containing both aliphatic, and aromatic amines yield materials that reconfigure and relax with a temperature dependence that follows Arrhenius behavior, consistent with PDKs being vitrimers.[27] The temperature-dependent stress-relaxation behavior for **PDK-6(TREN)** and **PDK-6(TREN:ODA)** shows activation energies of, respectively, 49 kJ mol^{-1} and 60 kJ mol^{-1} for solid-state bond exchange (Fig. 6).

Discussion

The closed-loop polymer life cycles emboldened by PDKs goes against that for conventional polymers, which are synthesized using irreversible bond-forming reactions that make it difficult and costly to recover the original monomers in high purity. Furthermore, while dynamic covalent polymers have been designed, in principle, around the ability to exchange bonds,[27] examples of energy-efficient depolymerization and chemical separations to obtain immediately reusable monomers are exceedingly rare; poly(diketoenamine)s may be privileged in this regard. Specifically, our work provides an important counterpoint to the observed stability of poly(ketoenamine)s to acid-catalyzed hydrolysis,[28,39–41] showcasing the importance of the second keto functionality in re-directing the foundational behavior of our materials toward more facile recycling, separation, re-manufacturing, and re-use in a fully closed-loop fashion (Supplementary Fig.

1). As the global binge on plastics accelerates,[42] PDKs stand out among a growing class of smarter plastics designed for chemical circularity.

Competing Interests

The authors declare the following competing interests: BAH and PRC are inventors on US provisional patent application 62/587,148 submitted by Lawrence Berkeley National Laboratory that covers poly(diketoenamine)s, as well as aspects of their use and recovery.

Data Availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information, and also available from the authors upon request. Crystallographic data for compounds **3**, **5**, and **TK-6** are available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference numbers 1891131, 1891132, and 189113, respectively.

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Author contributions: BAH and PRC designed and planned the project. PRC synthesized and characterized all poly(diketoenamine) materials and their recyclability. AMS synthesized small molecules and carried out experiments to measure activation energies for amine exchange. KEL carried out experiments to characterize the extent of network formation by ball-milling. BAH and PRC wrote the manuscript with contributions from all co-authors.

Figure Captions

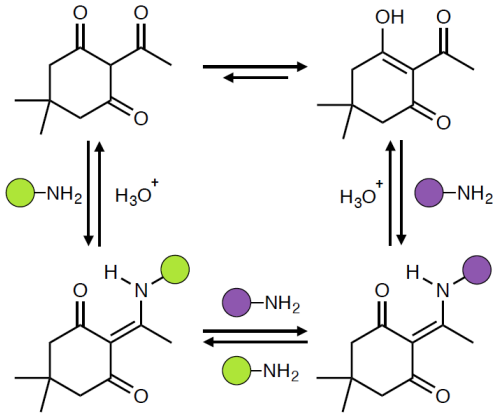
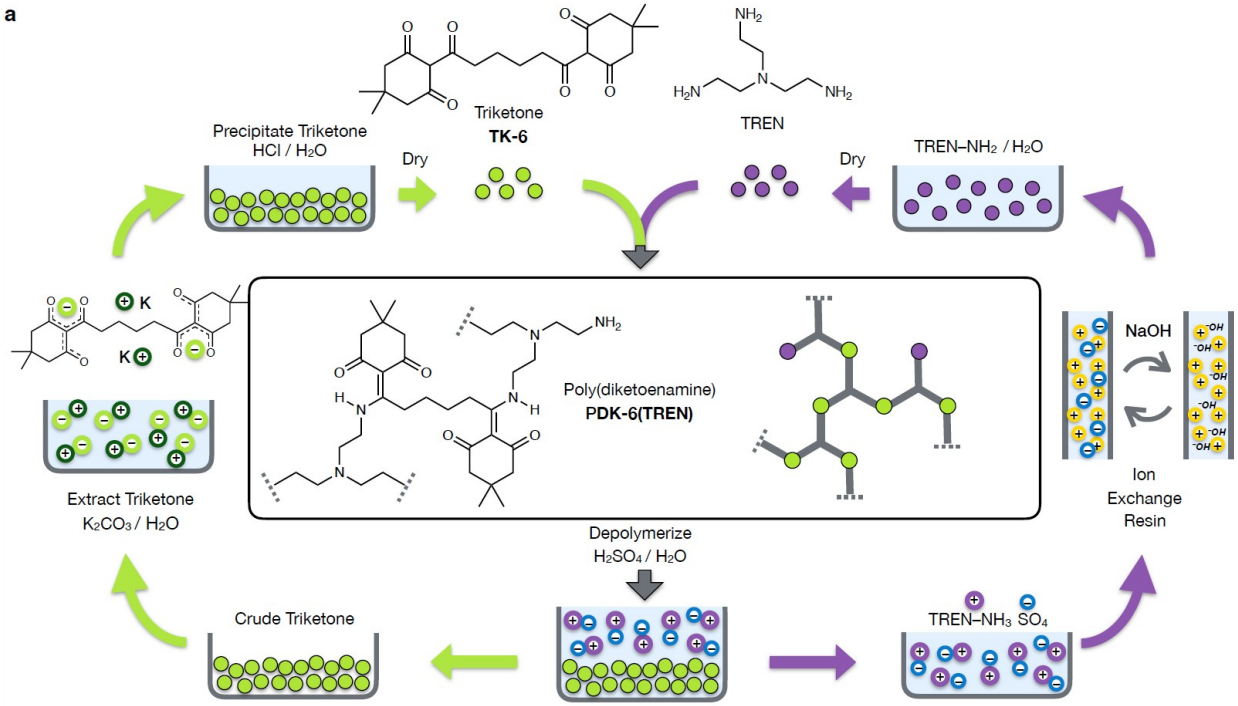


Fig. 1 | Reversible, dynamic covalent diketoenamine bonds. Diketoenamine bonds form spontaneously from triketones and both aromatic and aliphatic amines. Under strongly acidic conditions in water, the diketoenamine bond hydrolyzes to the triketone and an ammonium salt.



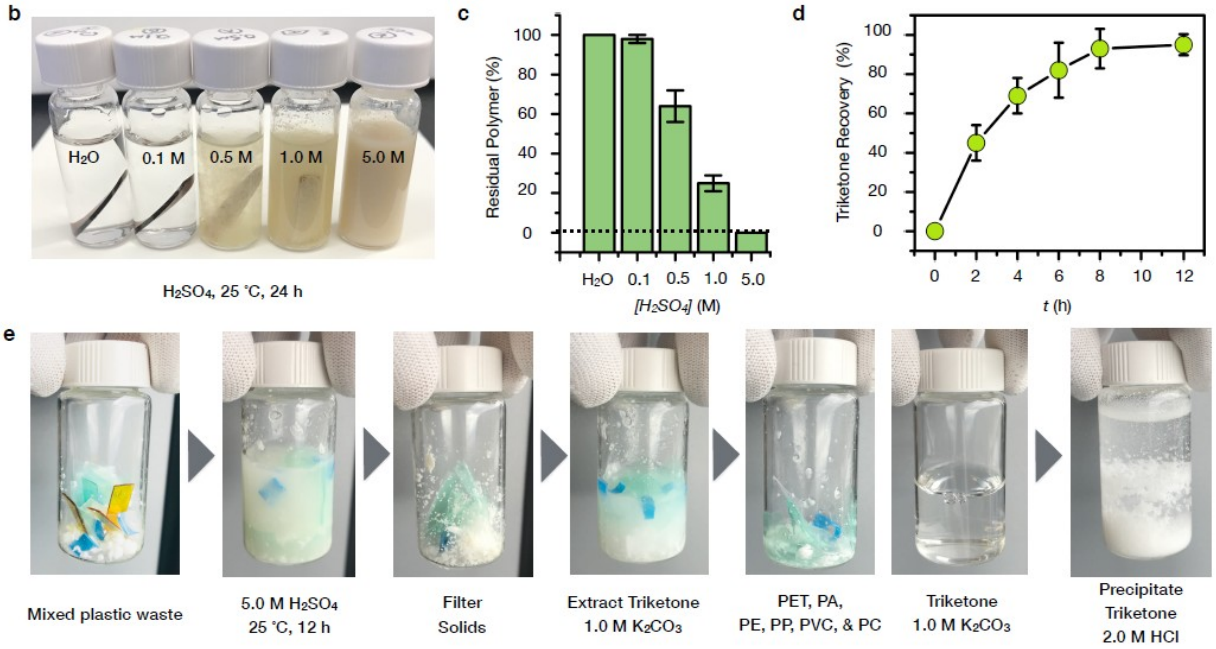


Fig. 2 | Closed-loop recycling from dynamic covalent poly(diketoenamine)s. a, Network PDKs (e.g., **PDK-6(TREN**)) are synthesized from polyamines (e.g., *tris*(2-aminoethyl)amine, TREN) and ditopic triketones (e.g., **TK-6**), and are hydrolyzed in strong acid. Both triketone and TREN monomers can be recovered and reused a closed-loop fashion using regenerative chemical processes. **b**, Photograph showing the depolymerization of **PDK-6(TREN)** in H_2SO_4 from 0–5.0 M, and **c**, corresponding data showing the amount of PDK remaining after 24 h at room temperature as a function of acid concentration. **d**, Triketone monomer recovery over time during **PDK-6(TREN)** depolymerization in 5.0 M H_2SO_4. **e**, Photographs showing orthogonal depolymerization of PDKs and triketone monomer recovery from mixed plastic waste containing poly(ethylene terepthalate) (PET), nylon-6,6 (PA), polyethylene (PE), poly(vinyl chloride) (PVC), and polycarbonate (PC). Data in **b** and **c** are the average of two trials; error bars are the standard deviation.

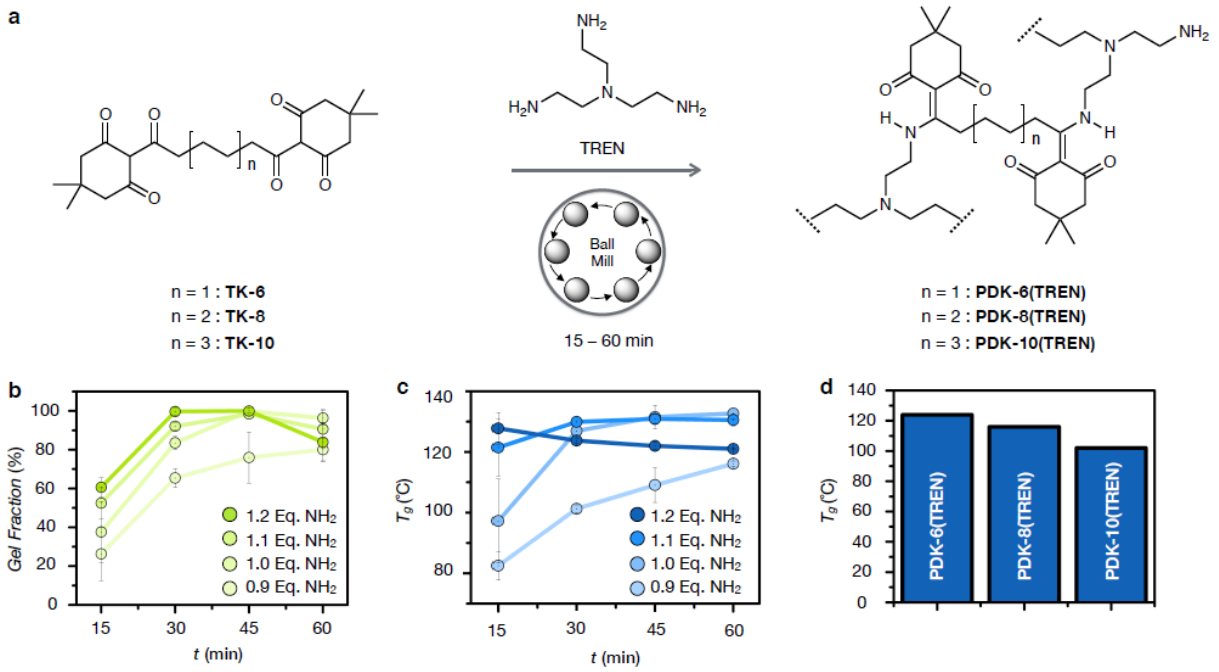


Fig. 3 | Synthesis of network poly(ketoenamine)s by ball-milling. **a**, Dynamic covalent PDKs are synthesized by ball-milling **TK-6–10** with TREN, yielding network polymers **PDK-6–10(TREN)**. Well-Controlled PDK network density is evidenced by repeatable trajectories for **b**, gel-fraction, and **c**, glass transition temperature (T_g), each as a function of ball-milling time and the mol% (Eq.) of amine functionality relative to triketone functionality in the formulation. Data are shown for **PDK-6(TREN)**. **d**, The observed T_g of different PDK networks decreases with increasing triketone spacer length. Data in **b** and **c** are the average of three trials; error bars are the standard deviation.

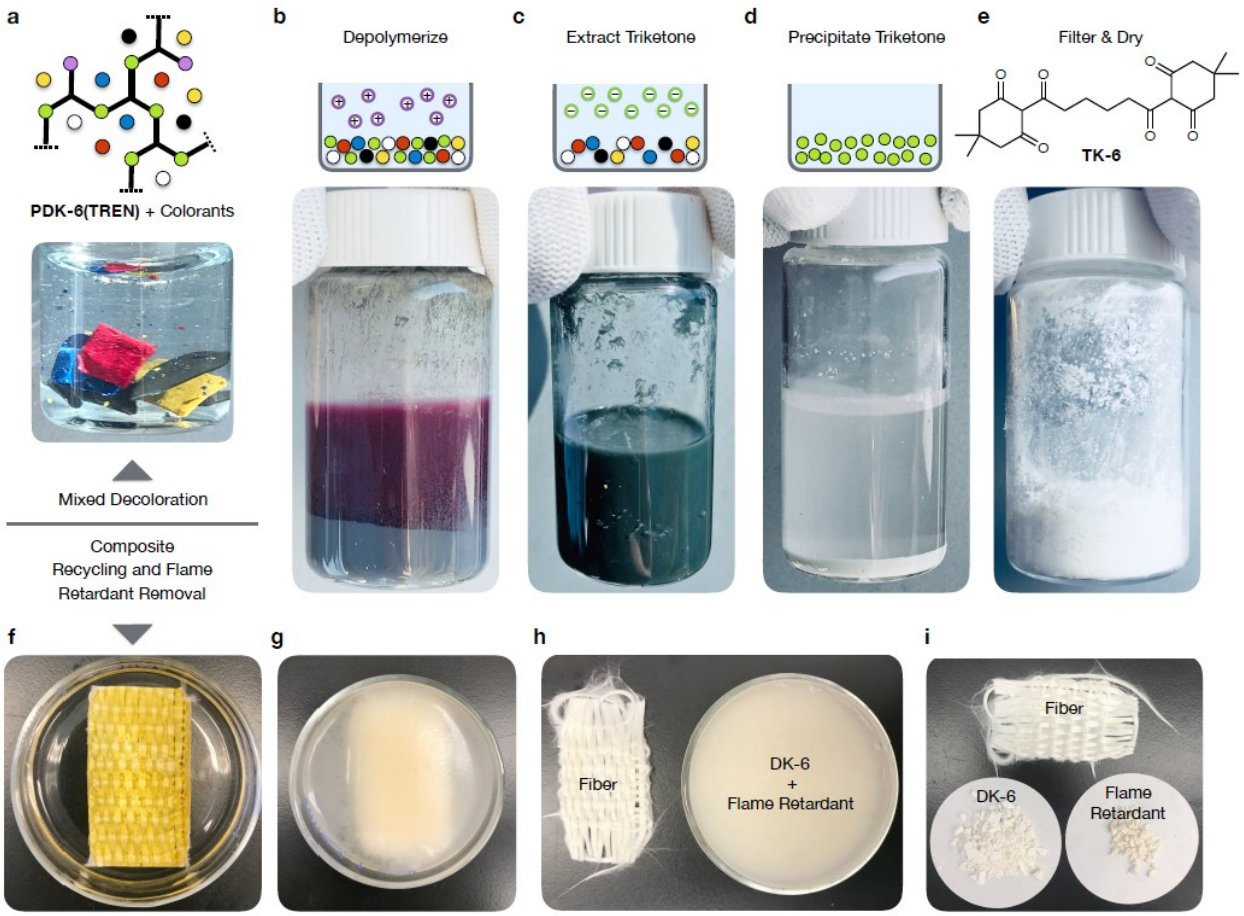


Fig. 4 | Mixed polymer decoloration, additive removal, and closed-loop recycling of fiber-reinforced composites. a, A mixed-color waste stream consisting of **PDK-6(TREN)** compounded with either carbon nanofibers, TiO_2, blue 3, yellow 3, or red 1 organic dyes. **b,** Red, blue, yellow, and black samples of **PDK-6(TREN)** were completely depolymerized at room temperature in 5.0 M H_2SO_4 to yield a solid mixture of **TK-6** monomer and pigments/additives. **c, TK-6** was extracted into aqueous base at room temperature and separated from additives by filtration. **d–e,** The basic extract was acidified, precipitating pure **TK-6** monomer. **f**, Fiberglass cloth, impregnated with **PDK-6(TREN)**, containing 25% (*w/w*) TPP flame retardant. **g–h**, Depolymerization of **PDK-6(TREN)** enables separation and recovery of undamaged fiberglass cloth. **i, TK-6** monomer is separated from the flame retardant additive in aqueous base allowing fiberglass cloth, flame retardant, and **TK-6** monomer to be isolated from each other.

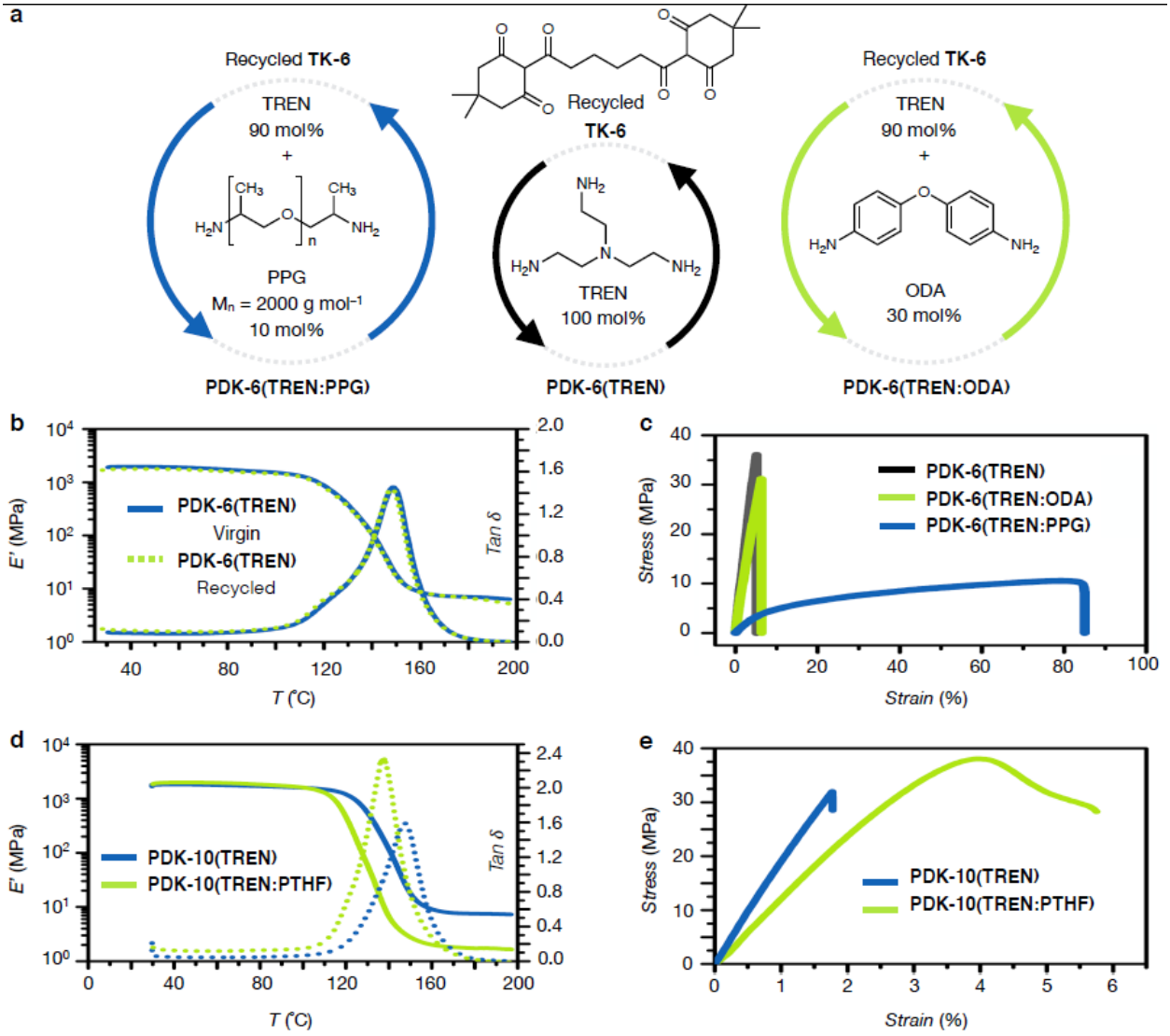


Fig. 5 | Re-formulation of poly(diketoenamine) networks. a, **TK-6** obtained through depolymerization of **PDK-6(TREN)** was used to re-formulate PDK networks with TREN, TREN alongside 4,4'-oxydianiline (ODA), and TREN alongside poly(propylene glycol) *bis*(2-aminopropyl ether) (PPG). **b**, Dynamic mechanical analysis (DMA) of **PDK-6(TREN)** showed nearly identical properties when formulated from either virgin or recycled **TK-6** monomer. **c**, Tensiometry for **PDK-6(TREN)**, **PDK-6(TREN:PPG)**, and **PDK-6(TREN:ODA)**. **d**, DMA and **e**, tensiometry for **PDK-10(TREN)**, and **PDK-10(TREN:PTHF)** containing 5 mol% poly(tetrahydrofuran) *bis*(2-aminopropyl ether) (PTHF).

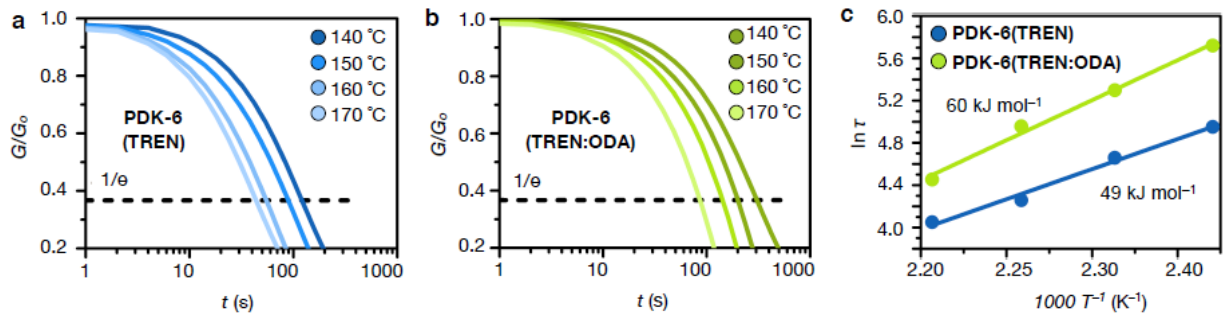


Fig. 6 | Dynamic covalent behavior of poly(diketoenamine) networks. a–b, Temperature-dependent stress relaxation for **PDK-6(TREN)** and **PDK-6(TREN:ODA)** polymers show Arrhenius-type behavior with **c**, activation energies of 49 and 60 kJ mol^{-1}, respectively.